

## Aromatic Nitration in Aqueous Nitric Acid

David J. Belson

Peterborough Regional College, Park Crescent, Peterborough, Cambridgeshire, PE1 4DZ

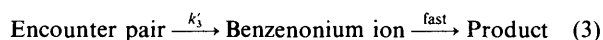
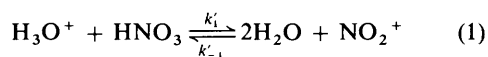
Alec N. Strachan\*

Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU

The rates of nitration of benzene, toluene, *p*-xylene, and mesitylene have been determined in aqueous nitric acid at concentrations between 24–41 mol % HNO<sub>3</sub> and at temperatures between 293–333 K. Plots of log<sub>10</sub> (*k*<sub>1</sub>/<sup>a</sup>HNO<sub>3</sub>) versus  $-H_0$ , where *k*<sub>1</sub> is the pseudo-first-order rate constant, <sup>a</sup>HNO<sub>3</sub> the activity of the nitric acid, and *H*<sub>0</sub> the Hammett acidity function, are linear, and confirm that the mechanism of nitration in aqueous nitric acid is similar to that in aqueous sulphuric acid. The slopes of such plots for *p*-xylene and mesitylene have values of ~2.0 whereas for benzene, toluene, and aromatic quaternary ammonium ions, the slopes have values closer to 3.0. The conclusion is drawn that with *p*-xylene and mesitylene the nitration is diffusion-controlled, but not so with the others.

The nitration activation energy, *E*, varies with both substrate and acid composition. At a given acid composition  $E_{\text{benzene}} > E_{\text{toluene}} > E_{\text{p-xylene}} > E_{\text{mesitylene}}$ . As in aqueous sulphuric acid, *E*, for a given aromatic decreases as the acid concentration is increased. The relative rates of nitration (benzene:toluene:*p*-xylene:mesitylene) at ~30 mol % HNO<sub>3</sub> and 25 °C are found to be 1:22:256:485. The relative rates, however, are not constant. They narrow as the temperature or acid concentration is raised. Finally it has been shown that the similarity between nitration in aqueous nitric acid and that in aqueous sulphuric acid extends to the reaction between nitronium ion and water. In both media this appears to involve two water molecules and not just one.

The findings of previous workers<sup>1–5</sup> suggest that the mechanism of aromatic nitration in aqueous nitric acid is identical to that in aqueous sulphuric acid<sup>6</sup> namely:



Application of the steady-state assumption leads to the following expression for the rate of nitration:

$$\frac{-d[\text{ArH}]}{dt} = \frac{k_1 k_2^a \text{H}_3\text{O}^+ \text{HNO}_3 [\text{ArH}]}{k_{-1} (\text{H}_2\text{O})^2 (1 + k'_{-2}/k'_3) + k_2 [\text{ArH}]} \quad (4)$$

where *a* denotes activity and [ ] concentration.

**Zero-order Kinetics.**—When  $k_2 [\text{ArH}] \gg k'_{-1} (\text{H}_2\text{O})^2 (1 + k'_{-2}/k'_3)$ , which will occur with reactive aromatics ( $k'_3 \gg k'_{-2}$ ) and high concentrations of aromatic ([ArH] large) or of nitric acid (<sup>a</sup>H<sub>2</sub>O small), (4) simplifies to:

$$\frac{-d[\text{ArH}]}{dt} = k_1^a \text{H}_3\text{O}^+ \text{HNO}_3 = k_0^a \text{HNO}_3 = k_0 \quad (5)$$

The rate of nitration is determined by reaction (1), and is zero order with respect to the aromatic substrate. This has been observed to be the situation with several reactive aromatics.<sup>1,2,5</sup> Moreover, with some of these, the zero-order rates (*k*<sub>0</sub> values) have been shown<sup>2</sup> to be equal to the rates of exchange of oxygen between nitric and water (*R* values), which would be expected if oxygen exchange occurs by reaction (1) and its reverse.

**First-order Kinetics.**—When  $k_{-1} (\text{H}_2\text{O})^2 (1 + k'_{-2}/k'_3) \gg k_2 [\text{ArH}]$ , which will arise at lower concentrations of aromatic substrate ([ArH] small) or of nitric acid (<sup>a</sup>H<sub>2</sub>O large), (4) simplifies to:

$$\frac{-d[\text{ArH}]}{dt} = k_2 \text{HNO}_3 [\text{ArH}] \quad (6)$$

with the second-order rate constant *k*<sub>2</sub> given by:

$$k_2 = k_1 k_2^a \text{H}_3\text{O}^+ / k_{-1} (\text{H}_2\text{O})^2 (1 + k'_{-2}/k'_3) \quad (7)$$

When nitric acid is in a large excess, which is invariably the case, first-order kinetics will be observed with a pseudo-first-order constant  $k_1 = k_2 \text{HNO}_3$ .

With reactive aromatics ( $k'_3 \gg k'_{-2}$ )

$$k_2 = k_1 k_2^a \text{H}_3\text{O}^+ / k_{-1} (\text{H}_2\text{O})^2 \quad (8)$$

Here the rate of nitration is diffusion-limited and determined by the rate of formation of the encounter pair [reaction (2)]. This appears to be the situation with mesitylene. Its *k*<sub>1</sub> values at 28.1, 29.7, and 31.4 mol % HNO<sub>3</sub> are only twice as great as those of *p*-xylene despite mesitylene being estimated to be 500 times more reactive than *p*-xylene.<sup>3</sup> Likewise the *k*<sub>1</sub> values of a number of other reactive aromatics at 30.4 mol % HNO<sub>3</sub> have been shown to be very similar in magnitude.<sup>5</sup> With less re-

$$k_2 = k_1 k_2 k_3^a \text{H}_3\text{O}^+ / k_{-1} k'_{-2} (\text{H}_2\text{O})^2 \quad (9)$$

active aromatics ( $k'_{-2} \gg k'_3$ ) and *k*<sub>2</sub> is now dependent on the reactivity of the aromatic, with reaction (3) being the rate-controlling step. This seems to be the case with benzene and toluene at nitric acid concentrations between 28.1 and 36.9 mol %, and with aromatic quaternary ammonium ions at concentrations between 33.4 and 100 mol %.

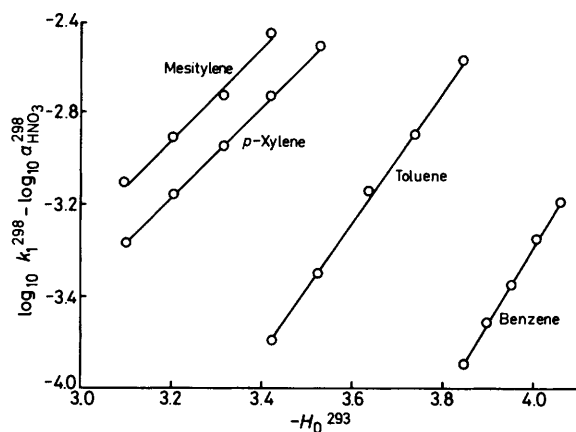


Figure 1. Plots of  $\log_{10} k_1 - \log_{10} a_{\text{HNO}_3}$  at 298 K versus  $-H_0$  at 293 K for benzene, toluene, *p*-xylene, and mesitylene

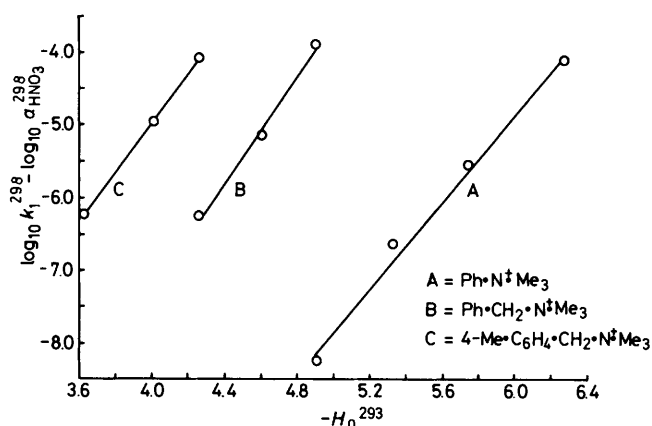


Figure 2. Plots of  $\log_{10} k_1 - \log_{10} a_{\text{HNO}_3}$  at 298 K versus  $-H_0$  at 293 K for aromatic quaternary ammonium ions<sup>5</sup>

However, although values of  $k_0$ ,  $R$ , and  $k_1$  for aqueous nitric acid and various aromatic substrates have been determined<sup>1-5</sup> and the rate profiles of  $R$  for oxygen exchange<sup>2</sup> and of  $k_1$  for quaternary ammonium ions<sup>5</sup> established, no correlations between rate constants and acidity functions similar to those for aqueous sulphuric acid<sup>6</sup> have been reported. Nor have activation energies and their dependence on acid concentration been determined. In aqueous sulphuric acid activation energies decrease with increasing acid concentration.<sup>7</sup> Finally no evidence has so far been produced to indicate whether one or two water molecules are involved in the reverse of the reaction (1). It was therefore with the aim of filling these gaps in our knowledge of aromatic nitration in aqueous nitric acid that the present work was undertaken.

## Experimental

**Materials.**—Benzene, toluene, and concentrated nitric acid (~70 wt%) were of AnalaR grade and *p*-xylene and mesitylene were of General Purpose Reagent grade. They were all supplied by British Drug Houses and used without further treatment.

**Preparation of Nitric Acid Solutions.**—A BS 718 Series L50 hydrometer was used to measure the relative density of the concentrated nitric acid. After correcting to 60 °C, the weight percentage composition was obtained from a graph of standard

data.<sup>8</sup> More dilute solutions were prepared by mixing together the requisite amounts of concentrated nitric acid and water. About 300 cm<sup>3</sup> were made up at a time. The weights of concentrated nitric acid and water, each measured to better than  $\pm 0.01\%$ , were used to calculate the resultant composition. This has been shown to be a more accurate method of establishing nitric acid concentrations than titration.<sup>9</sup>

**Kinetic Method.**—A small amount (2  $\mu\text{l}$ ) of aromatic liquid was added by microlitre syringe to ~20 cm<sup>3</sup> of nitric acid solution in a flask held in a water-bath controlled to  $\pm 0.1$  °C. Some of the mixture was quickly poured into a 1 cm cell and this inserted into the cell holder of a CE 272 u.v. spectrometer (Cecil Instruments Ltd.). Water from the water-bath circulated through the cell holder. With all four aromatics the absorbance of 340 nm was recorded at suitable intervals of time.

## Results and Discussion

First-order kinetics were observed in all runs. Values of the pseudo-first-order constant,  $k_1$ , determined in each case by Guggenheim's method,<sup>10</sup> are listed in Table 1. The activation energies, obtained by Arrhenius plots of the  $k_1$  data, are listed in Table 2, together with values of  $\log_{10} a_{\text{HNO}_3}$  at 298 K and the Hammett acidity function  $H_0$  at 293 K. The  $\log_{10} a_{\text{HNO}_3}$  values were interpolated from the data of Redlich *et al.*<sup>11</sup> using the relationship  $\log_{10} a_{\text{HNO}_3} = 2 \log_{10} \gamma_2 x_2$ , where  $\gamma_2$  and  $x_2$  are the activity coefficient and mole fraction respectively of nitric acid in H<sub>2</sub>O–HNO<sub>3</sub> mixtures. The  $H_0$  values were obtained by interpolation of those listed by Rochester.<sup>12</sup> They are 293 K values since these are known for the whole range of H<sub>2</sub>O–HNO<sub>3</sub> compositions, whereas those at 298 K have only been determined between 0–14 mol% HNO<sub>3</sub>.

**Acidity Function Correlations.**—(a) *First-order kinetics.* The second-order rate constant  $k_2 = k_1/a_{\text{HNO}_3}$ . Whether  $k_2$  is given by equation (8) or equation (9), it should be dependent on  $a_{\text{H}_3\text{O}^+}/(a_{\text{H}_2\text{O}})^2$  and hence on the acidity of the medium. In aqueous sulphuric acid the acidity dependence of  $k_2$  has been demonstrated by plotting  $\log_{10} k_2$  against various acidity functions  $H_0$ ,  $H_R$ , and  $(H_R + \log_{10} a_{\text{H}_2\text{O}})$ .<sup>6</sup> The most linear correlations have been found to be plots of  $\log_{10} k_2$  versus  $-H_0$ . Plots of  $\log_{10} k_1 - \log_{10} a_{\text{HNO}_3}$  ( $= \log_{10} k_2$ ) at 298 K versus  $-H_0$  at 293 K are shown in Figure 1. Their linearity with all four aromatics is added confirmation that the mechanism of nitration in aqueous nitric acid is similar to that in aqueous sulphuric acid. Figure 2 shows similarly constructed plots for aromatic quaternary ammonium ions using the data of previous workers.<sup>5,11,12</sup> Reasonable linearity is again observed.

The slopes of the lines in Figures 1 and 2 are listed in Table 3 together with the slopes of  $\log_{10} k_2$  versus  $-H_0$  observed in aqueous sulphuric acid.<sup>13</sup> It will be seen that in aqueous nitric acid the slopes for mesitylene and *p*-xylene are alike and lower than the slopes for toluene, benzene, and the quaternary ammonium compounds. This is a further indication that the nitration of mesitylene and *p*-xylene is diffusion-limited with their  $k_2$  values given by equation (8), whereas the  $k_2$  values of the less reactive aromatics are given by equation (9).

If  $k'_{-2}/k'_3$  decreases with increasing acid concentration, the increased slopes when equation (9) rather than (8) applies would be accounted for. This could be because as the acid becomes less aqueous the nitronium ion becomes less hydrated and closer to the aromatic in the encounter pair, leading to an increase in the rate of formation of the benzenonium ion [reaction (3)] relative to the rate of break-up of the encounter pair [reverse of reaction (2)]. Table 3 shows that in aqueous sulphuric acid a similar but less marked increase is observed

**Table 1.** Variation of the pseudo-first-order rate constant,  $k_1$ , for different aromatics with temperature and acid concentration

Aromatic	[HNO <sub>3</sub> ] mol%	10 <sup>4</sup> $k_1/s^{-1}$								
		293 K	298 K	303 K	308 K	313 K	318 K	323 K	328 K	333 K
Mesitylene	23.75			3.82	7.78	12.6	19.7	29.8	44.5	69.5
	25.16		5.57	10.4	15.9	26.7	37.2	47.9	72.9	
	26.62	5.68	11.1	18.2	30.4	43.0	52.2	76.8	92.1	
	28.13	13.4	21.5	35.9	45.7	57.8	91.7	134		
	29.74	40.3	51.4	76.8	106	141	196			
<i>p</i> -Xylene	25.16		3.03	6.15	10.0	16.6	27.6			
	26.62	3.73	6.25	11.2	17.1	28.9	40.5	61.1		
	28.13	7.67	13.0	21.4	30.6	49.5	64.1	98.2		
	29.74	17.0	27.2	42.9	59.8	90.8	128	184		
	31.38	38.5	56.0	86.1	123	169				
Toluene	29.74		2.34	4.01	7.12	11.7	17.6	27.0		
	31.38		5.84	9.79	15.4	22.7	31.5	50.7		
	33.15		16.9	24.9	35.9	51.8	68.0	89.7		
	34.97	30.4	38.2	55.8	77.4	98.7	131			
	36.85	72.4	98.9	132	186	225				
Benzene	34.97			2.76	4.53	6.81	10.7	15.9	22.6	33.2
	36.85		4.48	7.45	11.1	16.8	24.5	35.8	51.8	
	37.86		8.39	12.5	19.5	28.3	39.1			
	38.88	9.41	13.6	20.5	31.4	43.3	57.9	79.2		
	40.00		24.9	36.6	50.0	71.7	98.2			
41.02		40.7	58.4	81.3	111					

**Table 2.** Variation of the activation energy,  $E$ , with nitric acid concentration for different aromatics

[HNO <sub>3</sub> ] mol%	$-H_0$	log <sup>a</sup> HNO <sub>3</sub>	$E/kJ mol^{-1}$			
			Mesitylene	<i>p</i> -Xylene	Toluene	Benzene
23.75	3.00	-0.255	78.5			
25.16	3.10	-0.150	67.6	86.3		
26.62	3.21	-0.045	62.6	74.3		
28.13	3.32	+0.060	57.9	66.7		
29.74	3.425	0.163	51.2	62.1	78.6	
31.38	3.53	0.268		58.8	67.3	
33.15	3.64	0.373			53.7	
34.97	3.745	0.475			46.6	69.0
36.85	3.85	0.580			44.3	65.8
37.86	3.90	0.633				61.5
38.88	3.955	0.688				57.9
40.00	4.01	0.740				53.8
41.02	4.065	0.790				51.7

**Table 3.** Slopes of log<sub>10</sub>  $k_2$  versus  $-H_0$  at 25 °C

	Aqueous HNO <sub>3</sub>	Aqueous H <sub>2</sub> SO <sub>4</sub> <sup>13</sup>
Mesitylene	2.00	1.99
<i>p</i> -Xylene	1.98	1.80
Toluene	2.84	2.18
Benzene	3.25	2.31
( <i>p</i> -Methylbenzyl)trimethylammonium	3.27	—
Benzyltrimethylammonium	3.73	2.36
Phenyltrimethylammonium	2.93	—

between the slopes for the less reactive aromatics and those for mesitylene and *p*-xylene.

(b) *Zero-order kinetics.* When zero-order kinetics prevail and equation (5) applies, the acidity dependence of  $k'_0 = k'_1 \text{ } ^a\text{H}_3\text{O}^+$  might be expected to be different from that of  $k_2$ , whether  $k_2$  is given by equation (8) or equation (9). In aqueous sulphuric acid the slope of log<sub>10</sub>  $k'_0$  versus  $-H_0$  at 25 °C is lower than that of log<sub>10</sub>  $k_2$  versus  $-H_0$  and has the value 1.5.<sup>14</sup> Values

of  $k'_0 = k_0/{}^a\text{HNO}_3$  are not available over a range of nitric acid concentrations at 25 °C. However, the rates of exchange of oxygen between nitric acid and water ( $R$  values), which have been shown to be equal to  $k_0$  values,<sup>2</sup> have been determined at 0 °C as a function of acid concentration.<sup>2</sup> Some idea of how log<sub>10</sub>  $k'_0$  varies with  $-H_0$  in aqueous nitric acid can be obtained by plotting log<sub>10</sub>  $R$  (0 °C) - log<sub>10</sub> <sup>a</sup>HNO<sub>3</sub> (25 °C) versus  $-H_0$  (20 °C). Such a plot is shown in Figure 3. The slope of the line through the points has the value 2.10. If all the quantities ( $R$ , <sup>a</sup>HNO<sub>3</sub>,  $H_0$ ) were to be measured at the same temperature, because of the way activation energies vary with acid concentration (see below), we predict that the slope would be less and closer to that observed with aqueous sulphuric acid.

*Variation of Activation Energies with Acid Concentration.*— It is clear from Table 2 that experimental activation energies decrease as the acid concentration increases. The same phenomenon is observed in aqueous sulphuric acid,<sup>7</sup> and has been ascribed to  $\Delta H$  for reaction (1) becoming smaller as the

**Table 4.** Comparison of values obtained by different authors for the pseudo-first-order rate constant,  $k_1$ , for mesitylene at 25 °C

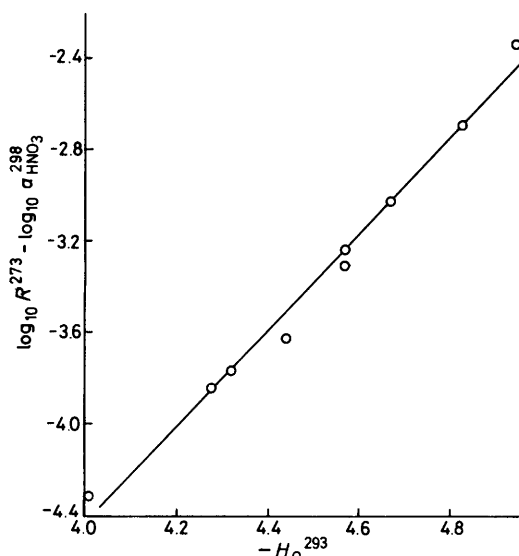
[HNO <sub>3</sub> ] wt %	[HNO <sub>3</sub> ] mol %	[HNO <sub>3</sub> ] mol dm <sup>-3</sup>	10 <sup>3</sup> $k_1/s^{-1}$		
			Hanson <sup>3</sup>	Ridd <sup>5</sup>	This work
57.81	28.13	12.5	4.03		2.15
59.70	29.74	13.0	10.7		5.14
61.55	31.38	13.5	21.2	5.23 <sup>a</sup>	10.1 <sup>b</sup>

<sup>a</sup> Interpolated from values at 60.4 and 63.7 wt % assuming  $\ln k_1$  versus wt % is linear over this limited concentration range. <sup>b</sup> Estimated from the  $k_1$  value for *p*-xylene assuming  $k_1$  (mesitylene)/ $k_1$  (*p*-xylene) = 1.8.

**Table 5.** Values of  $k_1$  (benzyltrimethylammonium),  $R$ , and <sup>18</sup>O<sub>2</sub> at different nitric acid concentrations

[HNO <sub>3</sub> ] mol %	$k_1$ (25 °C) <sup>5</sup> / s <sup>-1</sup>	$R$ (0 °C) <sup>2</sup> / mol % s <sup>-1</sup>	log <sub>10</sub> <sup>18</sup> O <sub>2</sub> (25 °C) <sup>11</sup>
60.9	3.53 × 10 <sup>-3</sup>	1.02 × 10 <sup>-1</sup>	-1.566
53.0	1.13 × 10 <sup>-4</sup>	1.06 × 10 <sup>-2</sup>	-1.304
45.6	5.13 × 10 <sup>-6</sup>	1.26 × 10 <sup>-3</sup>	-1.058
41.0	3.97 × 10 <sup>-7<sup>b</sup></sup>	3.37 × 10 <sup>-4</sup>	-0.905

<sup>b</sup> Estimated from the value for (*p*-methylbenzyl)trimethylammonium assuming relative rates are the same at 41.0 mol % HNO<sub>3</sub> as at 45.6 mol %.

**Figure 3.** Plot of  $\log_{10} R$  (0 °C)<sup>2</sup> -  $\log_{10} a_{\text{HNO}_3}$  (25 °C) versus  $-H_0$  (20 °C)

acid becomes more concentrated.<sup>4</sup> Unfortunately no data are available to indicate how  $\Delta H$  varies with concentration for aqueous nitric acid, but it is probable that the explanation for the phenomenon in this medium is the same as for that in aqueous sulphuric acid.

**Comparison of  $k_1$  Values.**—Values of the pseudo-first-order rate constant,  $k_1$ , for mesitylene obtained in this work are compared with values obtained by previous workers<sup>3,5</sup> in Table 4. It will be seen that the values of Hanson, Pratt, and Sohrabi<sup>3</sup> are consistently larger than those reported here by a factor of ~2.0. This is also true of their  $k_1$  values for benzene, toluene, and *p*-xylene when compared with ours. The most likely explanation for this discrepancy is that Hanson, Pratt, and Sohrabi's nitric acid concentrations were greater than their measurements indicated. They determined their acid

concentrations by titration.<sup>15</sup> This method has been shown<sup>9</sup> to give low values and to be less accurate than the gravimetric method used in this work.

Table 4 shows that the values of Draper and Ridd,<sup>5</sup> on the other hand, are smaller than those of this work by almost a factor of 2.0. Draper and Ridd had to correct their values upwards because of zero-order behaviour at the start of their runs. Undercorrection could explain why their values are low compared with ours.

**Relative Rates of Nitration.**—Hanson, Pratt, and Sohrabi<sup>3</sup> found the relative rates of nitration in aqueous nitric acid of benzene, toluene, *p*-xylene, and mesitylene to be 1:24:200:380, and similar to the relative rates of nitration of these substrates in aqueous sulpholane and aqueous nitromethane.<sup>16</sup> Table 1 shows that the relative rates found in this work are in broad agreement with previous findings. Thus combination of the  $k_1$  values at 298 K for benzene and toluene at 36.85 mol %, with those for toluene, *p*-xylene, and mesitylene at 29.74 mol %, gives relative rates of 1:22:256:485.

However, it is also clear that because the lower the reactivity, the larger the activation energy (Table 2), the reactivity ratios get smaller as the temperature is raised. Thus at 318 K combination of the  $k_1$  values for benzene and toluene at 34.97 mol %, with those of toluene, *p*-xylene, and mesitylene at 29.74 mol %, leads to relative rates of 1:12:89:136. Likewise it is clear from the slopes of the lines in Figure 1 that while the relative reactivities of benzene and toluene and of *p*-xylene and mesitylene remain fairly independent of acid concentration, being at 298 K ~1:22 and ~1:1.8 respectively, the ratio of the reactivity of *p*-xylene to that of toluene decreases as the acid concentration is increased. At 298 K the ratio falls from 11.6 at 29.74 mol % to 9.6 at 31.38 mol %. Thus the relative rates of nitration in aqueous nitric acid are not constant. They narrow as the temperature is raised or the acid concentration is increased.

**Reverse of Reaction (1).**—Combination of equation (5) and (9) leads to:

$$k'_0/k_2 = k_0/k_1 = (k'_{-1}k'_{-2}/k'_2k'_3)(a_{\text{H}_2\text{O}})^2 \quad (10)$$

A plot of  $\log_{10} k'_0/k_2$  versus  $\log_{10} a_{\text{H}_2\text{O}}$  should therefore be linear with a slope of 2.0. This has been observed to be the case in aqueous sulphuric acid,<sup>14</sup> confirming that the reverse of reaction (1) involves two water molecules and not just one. Table 5 lists  $k_1$  values at 25 °C for benzyltrimethylammonium at four widely different nitric acid concentrations,<sup>5</sup> together with the corresponding  $R = k_0$  values at 0 °C, interpolated from the data of Bunton and co-workers,<sup>2</sup> and  $\log_{10} a_{\text{H}_2\text{O}}$  values at 25 °C interpolated from the data of Reddich and co-workers.<sup>11</sup> Figure 4 shows a plot of  $\log_{10} R$  (0 °C) -  $\log_{10} k_1$  (25 °C) versus  $\log_{10} a_{\text{H}_2\text{O}}$  (25 °C). The slope is 2.1. It is very unlikely

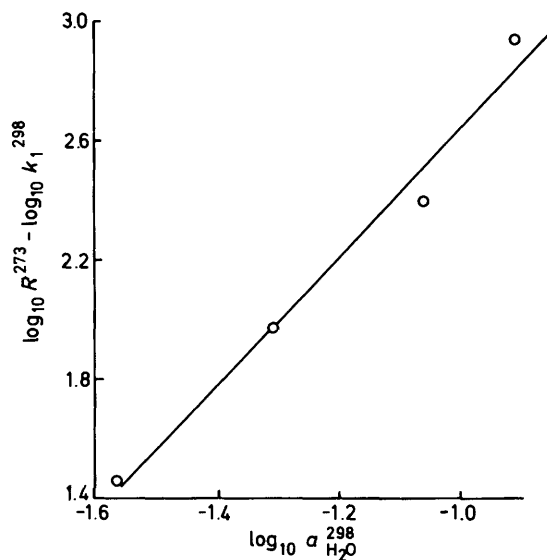


Figure 4. Plot of  $\log_{10} R (0^\circ\text{C})^2 - \log_{10} k_1 (25^\circ\text{C})^5$  versus  $\log_{10} a_{\text{H}_2\text{O}} (25^\circ\text{C})^{11}$

that if  $R (25^\circ\text{C})$  values were to be used the slope would be significantly different. Hence it can be concluded that equation (10) is as valid in aqueous nitric acid as it is in aqueous sulphuric acid, and that in both media the reverse of reaction (1) involves two water molecules.

#### Acknowledgements

We thank the Royal Society of Chemistry for a Research Fund grant to D. J. B. and Peterborough Regional College for the use of facilities.

#### References

- 1 E. D. Hughes, C. K. Ingold, and R. I. Reed, *J. Chem. Soc.*, 1950, 2400 and 2441.
- 2 C. A. Bunton, E. A. Halevi, and D. R. Llewellyn, *J. Chem. Soc.*, 1952, 4913; C. A. Bunton and E. A. Halevi, *ibid.*, p. 4417; C. A. Bunton and G. Stedman, *ibid.*, 1958, 2420.
- 3 C. Hanson, M. W. T. Pratt, and M. Sohrabi, 'Industrial and Laboratory Nitrations,' eds. L. F. Albright and C. Hanson, American Chemical Society, Washington, 1976, p. 225.
- 4 J. P. Field and A. N. Strachan, *Ind. Eng. Chem., Prod. Res. Dev.*, 1982, **21**, 352.
- 5 M. R. Draper and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1981, 94.
- 6 K. Schofield, 'Aromatic Nitration,' Cambridge University Press, Cambridge, 1980, ch. 3.
- 7 J. W. Chapman and A. N. Strachan, 'Industrial and Laboratory Nitrations,' eds. L. F. Albright and C. Hanson, American Chemical Society, Washington, 1976, p. 219.
- 8 'Lange's Handbook of Chemistry,' 11th edn., McGraw-Hill, New York, 1973.
- 9 D. J. Belson, *Sch. Sci. Rev.*, 1984, 333.
- 10 E. A. Guggenheim, *Philos. Mag.*, 1926, **1**, 538.
- 11 O. Redlich, W. E. Gargrave, and W. D. Krostek, *Ind. Eng. Chem. Fundam.*, 1968, **7**(2), 211.
- 12 C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970, p. 47.
- 13 A. R. Katritzky, B. Terem, E. V. Scriven, S. Clementi, and H. O. Tarhan, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1600.
- 14 R. B. Moodie, K. Schofield, and P. G. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1979, 133.
- 15 M. Sohrabi, Ph.D. Thesis, University of Bradford, 1972.
- 16 J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc.*, 1969, 1.

Received 16th November 1987; Paper 7/2023